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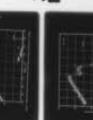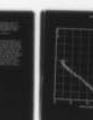
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BY   DONALD G. SIMONS   DAVID J. LAND
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RESEARCH AND TECHNOLOGY DEPARTMENT

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Proton backscatter analysis has been used to study lithium-boron residues which have been produced by a chemical process designed to extract the free lithium phase from lithium-boron alloys. On the two samples studied there is no evidence of the presence of Li on those surfaces which were in direct contact with the extraction chemicals. This depletion appears to be at least 3.5 μm deep. Measurements on the inside surfaces show that Li is present in a concentration which is in excess of the bound Li content of the samples.

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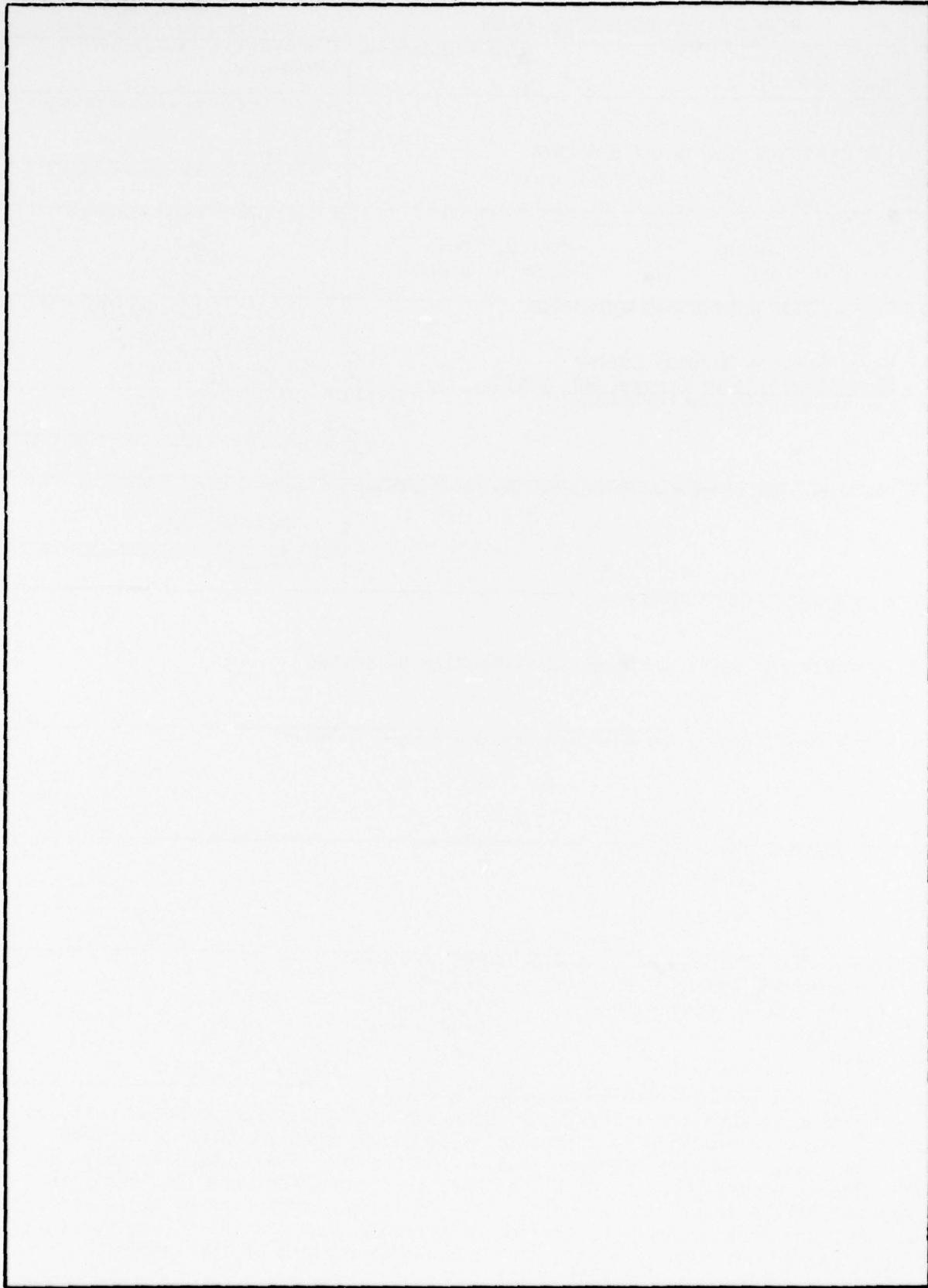
SUMMARY

Proton backscatter analysis has been used to study lithium-boron residues which have been produced by a chemical process designed to extract the free lithium phase from lithium-boron alloys. On the two samples studied there is no evidence of the presence of Li on those surfaces which were in direct contact with the extraction chemicals. This depletion appears to be at least 3.5 μm deep. Measurements on the inside surfaces show that Li is present in a concentration which is in excess of the bound Li content of the samples.
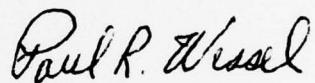
Paul R. Wessel

PAUL R. WESSEL
By direction

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INTRODUCTION

The use of a Li-B alloy as a possible anode material for batteries is currently being studied by this laboratory. This alloy has a potential safety advantage over other Li bearing materials since it may provide an anode with a relatively high concentration of free lithium in a high melting point matrix of a lithium-boron alloy. One of the problems is to determine the phase composition of these lithium rich alloys by determining the relative amounts of free and bound lithium. A technique introduced by Kilroy and Angres[1] involves the chemical extraction of the free lithium from the Li-B alloys and the quantitative determination of its concentration. The extraction medium consists of solutions of dry napthalene in dry tetrohydrofuran (THF). A description of the procedure is given in reference 1. The extraction procedure is continued until no additional lithium is found in the leaching medium. By knowing how much Li and B were used in the manufacture of the Li-B alloy and how much Li is removed by the extraction procedure, the amount of Li remaining in the residue is thus measured, and the stoichiometry of the residual alloy is inferred. It was concluded from this investigation that the free Li phase may be removed from the Li-B alloys by this process, and the empirical formula of $Li_{1.15\pm.05}B_{1.00}$ was inferred for the residual compound. It was the purpose of the investigation reported herein to use ion-beam backscatter techniques to study Li-B residues produced by Kilroy and Angres as an alternate procedure for determining their Li-B ratio.

METHOD

Ion-beam scattering is a valuable tool for determining materials surface composition. By measuring the energy spectra of monenergetic ions scattered from solid targets at a fixed angle one may determine the target constituents and under proper circumstances the stoichiometry at or near the surface. The energy of an ion of incident energy E_{inc} and mass M_1 which has been scattered by a target atom of mass M_2 through laboratory angle θ is given by

$$E_{scatt} = K E_{inc},$$

where the kinematic factor K is

$$K = \left[\frac{M_1 \cos\theta + \sqrt{M_2^2 - M_1^2 \sin^2\theta}}{M_2 + M_1} \right]^2 .$$

The kinematic factor for several target atoms pertinent to this problem for projectiles of protons and helium ions scattered at a lab angle of 155° is given in Table 1.

1. W. P. Kilroy and I. Angres, "Determination of Free Lithium in Lithium-Boron Alloys" NSWC/WOL TR 77-129 (April 1978).

Table 1. Kinematic Factors for Protons and Helium Ions Scattered
at 155° by Selected Target Atoms

Element	Mass	K(Protons)	K(He)
Li	6.939	0.572	0.080
B	10.81	0.700	0.226
C	12.01	0.726	0.266
N	14.01	0.760	0.325
O	16.00	0.786	0.377

Thus, a 1000 keV proton scattered from Li at 155° has an energy of 572 keV while the energy is only 80 keV for a 1000 keV He ion. Because of this low kinematic factor for He on Li, this study was made with protons only.

Scattering from atoms inside the target as well as from those on the surface contribute to the particle spectrum from a bulk sample. The particles scattered from atoms inside the target have a lower energy than those scattered from atoms nearer the surface. The maximum energy is due to those scattering events which occur with atoms at the target surface. Furthermore the scattered spectrum from a composite target is a superposition of particles scattered from each constituent, each with a different kinematic factor. Thus, an energy spectrum of 1000 keV protons scattered from a Li-B composite at 155° shows a sharp reduction in the number of counts as the energy of the scattered particle is increased above 572 keV and another sharp decrease as the energy is increased above 700 keV. The first reduction is due to scattering from Li and the second from B. The intensity of the spectrum at these two edges is due to their concentration at the sample surface.

The counting rate for an incident particle of charge Z_1 scattered at an angle scattered from a thin layer in a target with atomic number Z_2 is given by

$$C = I\sigma(E,\theta,Z_1,Z_2) \, N \, td\Omega\varepsilon \; ,$$

where I is the number of incident ions per second, σ the differential scattering cross section, N the number of target atoms per cm^3, t the target thickness, $d\Omega$ the detector solid angle and ε the detector efficiency. For cases in which scattering is from a composite target, I, t, θ, $d\Omega$ and ε remain constant for scattering from each constituent. Thus, the relative concentration of atoms in a target of atomic number Z_A and Z_B is given by

$$\frac{N(Z_A)}{N(Z_B)} = \frac{C(Z_A)}{C(Z_B)} \; \frac{\sigma(Z_B)}{\sigma(Z_A)} \; ,$$

where $C(Z_A)$ and $C(Z_B)$ are the intensities of the scattered particles from constituents Z_A and Z_B respectively and are obtained from the backscatter spectrum. The scattering cross section $\sigma(E,Z)$ is known from other sources and, in general,

is calculated directly from Rutherford scattering theory. When protons are used as a probe on targets with low atomic number (Li and B in this case), Rutherford scattering is not the only process which can contribute to the scattering spectrum. Nuclear elastic scattering and possibly other nuclear reactions must be considered.

RESULTS

Measurements were carried out at laboratory scattering angles of 155° using 1 MeV protons from the NAVSWC 2.5MV Van de Graaff Accelerator. The scattered protons were detected using a silicon surface barrier detector and the proton spectra were recorded in a multichannel analyzer. Targets of reported residue composition of $Li_{1.06}B_{1.00}$ and $Li_{5.04}B_{4.00}$ were investigated. Only those results from the former target are reported here since those from the latter give no significant qualitative differences from the former.

Spectra from two parts of the target were taken, one from the outer surface of the sample as supplied to us and one from an inner surface after the sample was cut open. The two spectra are shown in Figures 1 and 2 respectively. The features of the two spectra are decidedly different and bear significant conclusions for the extraction process. In Figure 1 we see a sharp edge due to scattering from B (700 keV protons) at the surface of the sample but no apparent feature due to scattering from Li (572 keV). Thus, there appears to be little or no Li at the surface of the sample. This surface was in direct contact with the extraction chemicals. On the other hand the backscatter spectrum, Figure 2, taken from the inside surface of the same sample shows strong features due to scattering from both Li and B indicating presence of both. In addition, the presence of oxygen is also quite evident from this sample. This feature is not surprising if one were to assume that "free" Li was still present in the sample's interior and that it oxidized readily once the sample was cut open. This change was observed visually; immediately after cutting the sample open, the inside surface had a silver appearance which slowly turned greyish white on exposure to the atmosphere.

Under the assumption that the major contributing factors in the intensity of the proton spectrum are the Rutherford and nuclear elastic scattering probabilities, the stoichiometry of the surface was determined. The elastic scattering cross sections of Warters et al[2] and Bashkin and Richards[3] for Li, Taufest and Rubin[4] for ^{11}B and Laubenstein and Laubenstein[5] for ^{16}O were used. Using equation 1 and $\sigma = \sigma_{elastic} + \sigma_{Rutherford}$ the relative concentrations of Li:B:O for the interior surface was determined to be in the ratio of 1.4:1.0:0.6. This ratio is in contrast with the Li:B ratio of 1.15:1.00 as reported by Kilroy and Angres.

2. W. D. Warters, W. A. Fowler and C. C. Lauritsen, Phys. Rev. 91, 917 (1953).

3. S. Bashkin and H. T. Richards, Phys. Rev. 84, 1124 (1951).

4. G. W. Tautfest and S. Rubin, Phys. Rev. 103, 196 (1956).

5. R. A. Laubenstein and M. H. W. Laubenstein, Phys. Rev. 84, 18 (1951).

The determination of the Li content at the surface of the uncut sample was done statistically since the spectrum does not show any clear evidence of Li. Under the assumption that if Li were on the surface its presence would have been detected if the count at 576 keV were three standard deviations above the count actually obtained, the residual compound of $Li_{<0.12}B_{1.00}$ was determined. This value also is not consistent with the reported values of $Li_{1.15}B_{1.00}$.

CONCLUSIONS

The ion beam analyses of the two Li-B alloy samples which were supplied to us do not show the presence of Li on those surfaces which were in direct contact with the extraction chemicals. This depletion is at least 3.5 μm deep into the samples. In addition, our measurements on the inside surfaces of these samples show that the Li:B ratio (1.4:1) is in excess of the reported value for the bound Li phase (1.15:1). On the basis of these measurements we conclude that all of the Li (free and bound) was removed from the outer surfaces of these samples. We also conclude that the chemical diffusion was insufficient for effective Li extraction from their interiors. These results appear to be in direct contradiction with the claim that the chemical extraction process only removes the free Li from these alloys and that there is sufficient diffusion and porosity to ensure uniform removal of all of the free Li from the bulk samples. However, since our measurements were made on a limited number of samples, any general conclusions to be made which would resolve this apparent contradiction must be reserved until a more comprehensive set of measurements can be made.
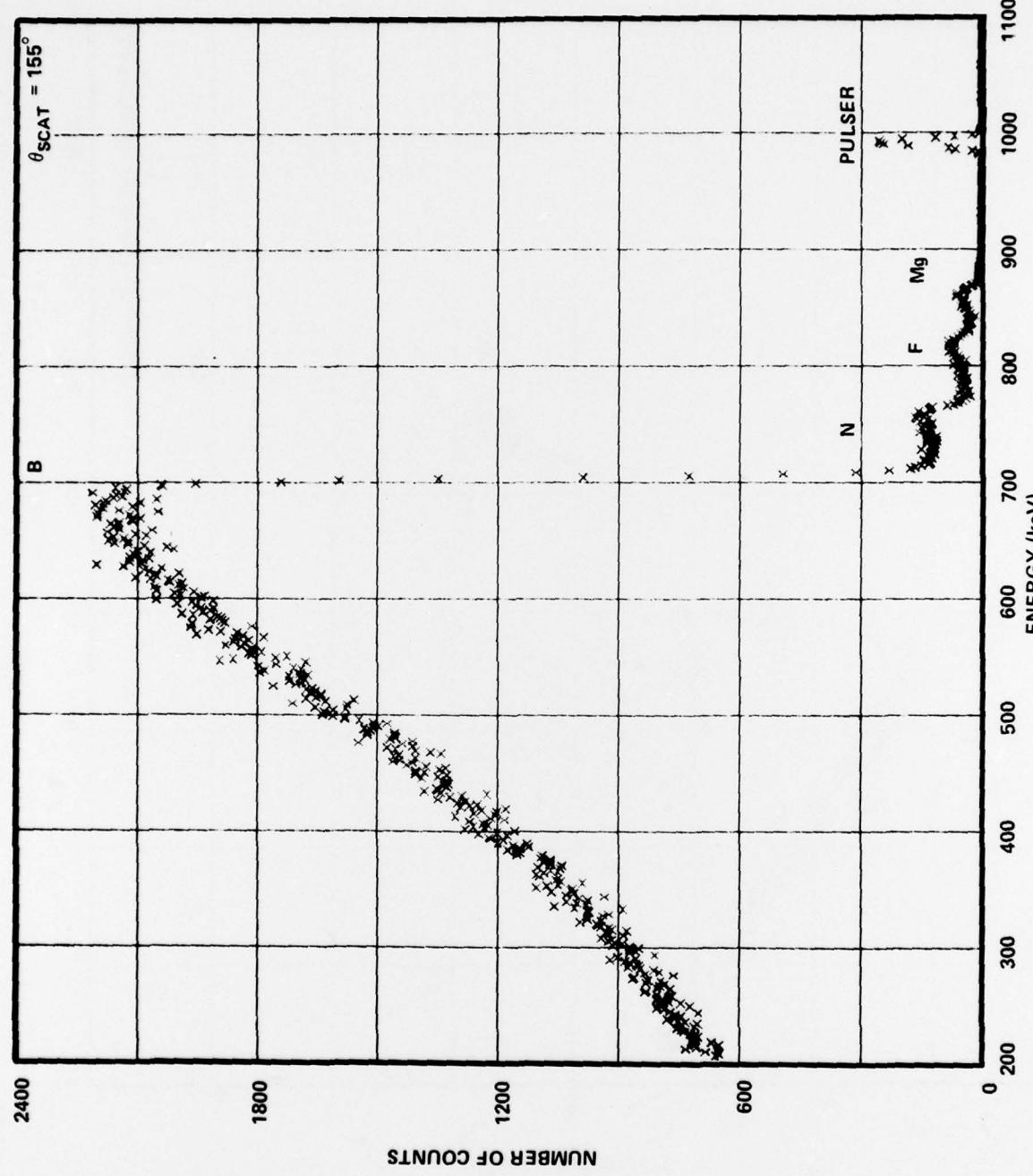
FIGURE 1. ENERGY SPECTRUM OF 1.0 MeV PROTONS SCATTERED FROM THE EXTERNAL SURFACE OF Li-B RESIDUE.
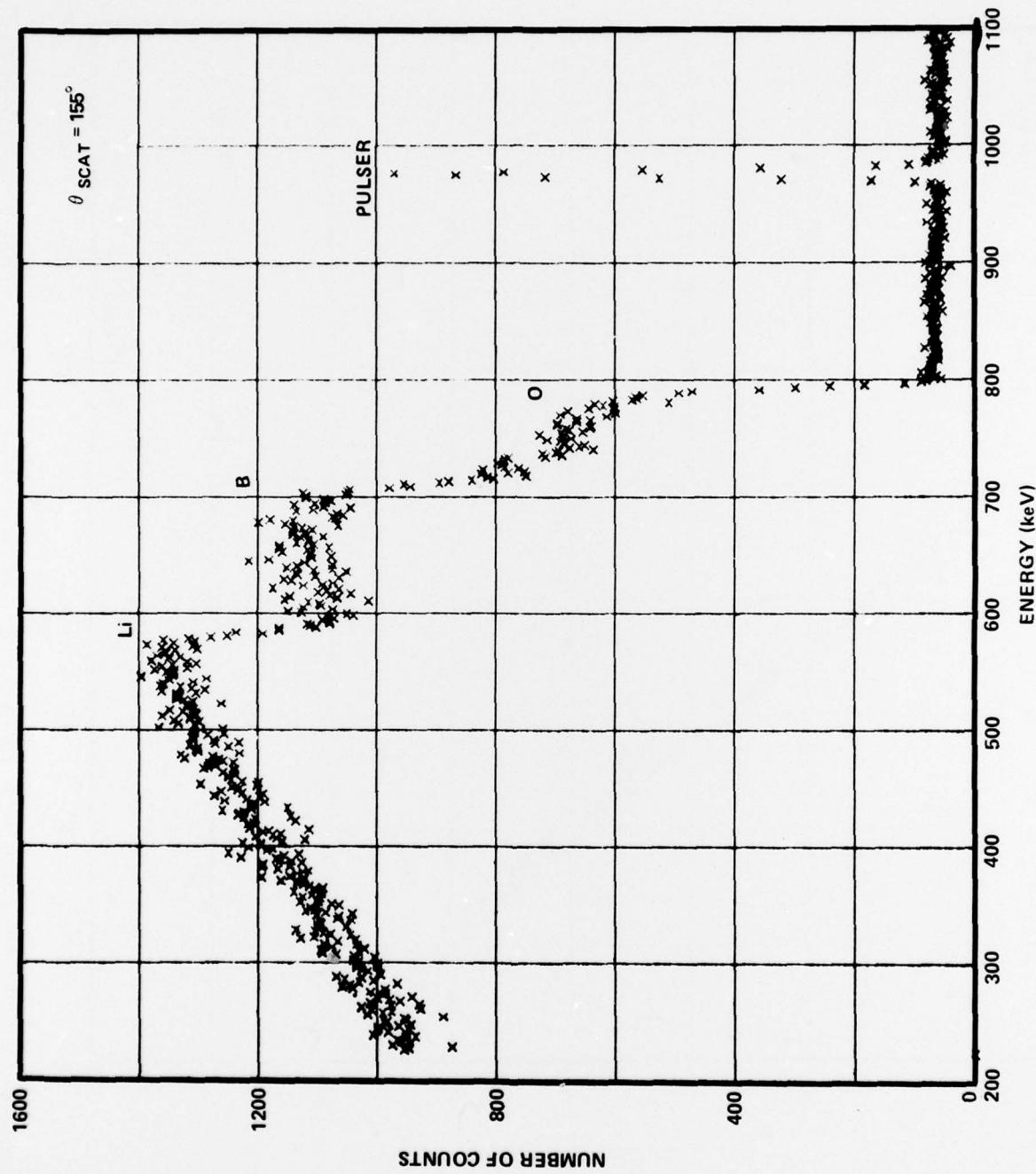
FIGURE 2. ENERGY SPECTRUM OF 1.0 MeV PROTONS SCATTERED FROM EXPOSED INTERNAL SURFACE OF Li-B RESIDUE.

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2. W. D. Warters, W. A. Fowler and C. C. Lauritsen, Phys. Rev. 91, 917 (1953).

3. S. Bashkin and H. T. Richards, Phys. Rev. 84, 1124 (1951).

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